The Role of Bedrock Geology in the Aqueous Chemistry of Cantabrian Rivers

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by

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Abstract

The relationship between the bedrock and the aqueous chemistry of rivers in northern Spain has yet to be investigated. This study's goal is to do just that, to relate the geology of the bedrock to the chemistry of each river and to determine which minerals in the bedrock are being weathered. While the majority of the rivers have very similar chemistries and flow through fairly similar lithologies, one river stands out from the rest. This river, the Ría de Villaviciosa, is the only river that flows through an evaporite deposit, and its chemistry reflects this difference in lithology. It is the only river that has an excess of Cl^- when compared to Na^+, and it is the only river not dominated by bicarbonate. The Ría de Villaviciosa also has a high concentration of lithium when compared with the other rivers. This could be due to the presence of a lithium evaporite mineral or due to lithium substitution for magnesium and/or iron.

Using PHREEQC, a geochemical modeling software, to determine the minerals being weathered by each river, it can be seen that the Ría de Villaviciosa is the only river that is oversaturated with respect to any mineral; it is oversaturated with respect to quartz. This could be misleading, as the concentration of aluminum was not measured in this study, so aluminosilicate weathering is not considered by PHREEQC as an input for SiO_2 in these rivers.

These rivers all flow through primarily sedimentary rocks, but the differences in bedrock lithologies can be seen in the chemistry of the rivers. Even slight differences in lithologies are reflected in slight difference in chemistries of each river, and significant differences in lithologies show significant differences in chemistries of the rivers.

Introduction

Northern Spain is a geologically complex region dominated by sedimentary rocks. There are also metamorphic rocks that come from sedimentary parent rocks. Although the majority of the rocks are sedimentary, there is a wide variety of types of sedimentary rocks in the drainage basins of each different river. The chemistry of rivers in this area (in this study, Asón, Sella, Villaviciosa, Narcea, and Nalón) has never been related back to the geology of the region, so it is not known what minerals are being weathered by each river. The variety of sedimentary rocks makes this an excellent region to investigate the effect of bedrock geology on river chemistry.

This type of work has yet to be done on rivers in Spain, but it has been done in many other regions. Stallard and Edmond (1987) related the chemistry of the Amazon River to the geology of its drainage basin, and Goldsmith et al. (2008) did the same with rivers in New Zealand. The purpose of this study was the same as the previous studies: to determine the relationship between the bedrock geology and the aqueous chemistry of the rivers. Through the analysis of the water chemistry by using the geochemical modeling software PHREEQC, the minerals being weathered can be determined.

Geologic Setting

Northern Spain is a geologically complex region. While there are many faults in this region, the most noticeable geologic feature of this part of northern Spain is the Cantabrian Cordillera. This region is part of “Variscan Spain” because it was not affected by the Alpine orogeny (Gibbons & Moreno, 2002). While it was not affected by the Alpine orogeny events, it was affected by some sort of mountain building, due to the fact that there are mountains in this region. The study area's location in "Variscan Spain," as well as its location in relationship to Spain as a whole can be seen in Figure 1.

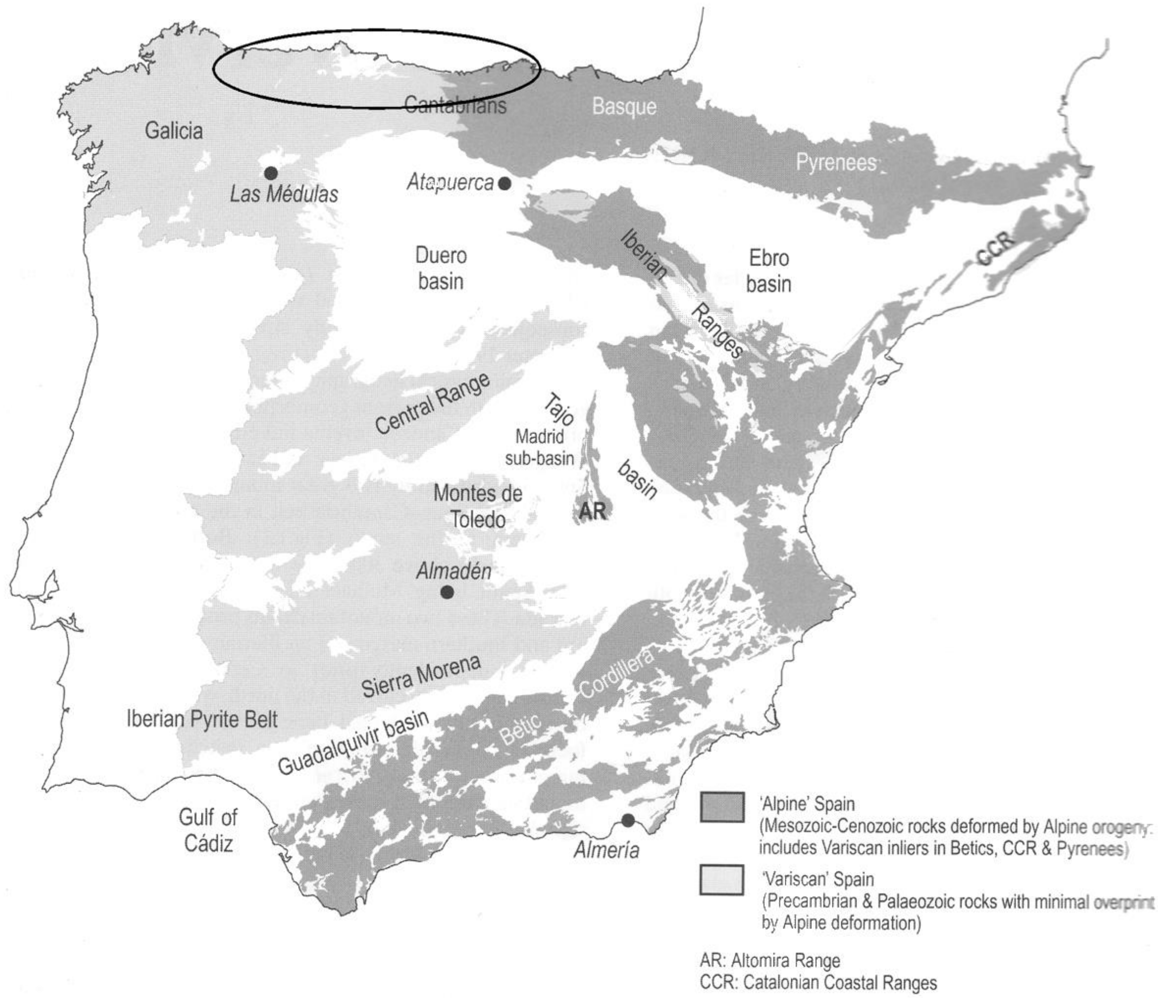


Figure 1. A map of Spain with the study area circled. Adapted from Gibbons & Moreno (2002).

The bedrock of northern Spain is primarily composed of sedimentary rocks. There are some areas of metamorphic rocks, which, in this region, are slate and quartzite. There are very few igneous rocks; the igneous rocks are always found in porphyritic dikes. The compositions of these igneous rocks are not known. There are also clay minerals, which are the result of weathering other minerals. Near the mouth of the each river, there are many different types of nonconsolidated sediments. These unconsolidated sediments are all geologically recent.

Four of the five rivers studied—Río de Asón, Río de Sella, Río Nalón, and Río Narcea—run through fairly similar lithologies. The major components of these lithologies are sandstone and carbonates. The fifth river, Ría de Villaviciosa, runs through a large evaporite deposit. This summary is the most prevalent lithologies of each river; each river flows through additional rock types. A set of tables detailing the exact lithologies can be found in the appendix. Unless otherwise stated, all of the descriptions were developed from maps made by the *Instituto Geológico y Minero de España* (Spain's Geologic Survey).

Asón: The Río de Asón flows mainly through sandstone and carbonate of Jurassic and Cretaceous ages. It also flows through clay, conglomerate, and marl of the same age.

Sella: The Río de Sella flows through carbonates of Cambrian age, and through glauconite-containing sandstone of Cambrian/Ordovician age; the glauconite-containing sandstone is found near a thrust fault. It also flows through Ordovician quartzite and siltstone; the quartzite is located near a fault, but the type of fault is not specified on the map. It flows through Carboniferous-age black calcite, carbonates, and rhythmites of Jurassic age. Finally, the Río de Sella flows through Cretaceous quartzarenite, sandstone, limestone, and siltstone.

Narcea: The Río Narcea flows through Devonian carbonate, sandstone, and slate, and through Carboniferous limestone, slate, and sandstone. Some of the Devonian slate is located near a thrust fault, but not all of it is. Some of the sandstone contains iron. It also flows through a porphyritic dike of an unknown age and of an unknown composition.

Nalón: The Río Nalón flows through the same lithologies as the Río Narcea. In addition, it flows through Cambrian/Ordovician slate and quartzite; some of this slate contains kaolinite. It flows through a mine region, where Ordovician white quartzite is mined. There are two mines in this region; one mine was inactive when this map was printed in 1972, and the other was still active when this map was made. The Río Nalón also flows through a region containing black shales of Silurian age. It also flows through a region of Tertiary clay and white limestone.

Villaviciosa: The Ría de Villaviciosa flows through Jurassic carbonate. It also flows through a region of red clays, calcite conglomerates, and calcite from the Triassic. This river is the only one of these five rivers that flows through an evaporite deposit. According to Martínez-García et al. (1998), these evaporites are gypsum—$CaSO_4 \cdot 2H_2O$—and anhydrite—$CaSO_4$; however, there is a possibility that other evaporites are present in this area. It also flows through a coal deposit of Carboniferous age.

Method

Water samples from each river were taken in September 2011 when the rivers were at base flow. These samples were collected in new, low-density polyethylene (LDPE) bottles that had been soaked in deionized water (18 MΩ). In the field, each bottle was rinsed out with river water thrice before the sample was collected. In this study, the pH of the water was not measured. To prepare the samples for analysis, they were filtered through a 47 mm diameter (nominal pore size of 0.4 μm) polycarbonate filter directly into an acid washed 60 mL LDPE bottle for cation analysis and a 60 mL LDPE bottle for anion analysis. Filter blanks were made by filtering 18 MΩ water into new, clean LDPE bottles using the same methods as used in collecting samples. Prior to collecting the samples, trip blanks were made with 18 MΩ water in new, clean LDPE bottles. After all of this was completed, the samples were shipped back to Ohio State and chilled at approximately 4°C until analysis.

Upon return, each filtered sample for cation analysis was acidified with trace metal grade HNO_3 to pH 2-3 for preservation. Using the methods of Welch et al. (1996), major ion concentrations for cations (Li^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}) and anions (F^-, Cl^-, and SO_4^{2-}) were determined using a Dionex-120® ion chromatographer via ion chromatography. Five replicate check standards were used per run to check precision. The relative standard deviations of these checks were usually better than $\pm$3% and never greater than $\pm$6%. Dissolved Si concentrations were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES). External standards and check standards were run every 3-4 samples to account for instrument drift. Triplicate analyses did not reveal RSDs greater than $\pm$5%.

After the samples were analyzed, the ion concentration data were entered into PHREEQC (Parkhurst & Appelo, 2013). PHREEQC stands for pH (PH), redox (RE), equilibrium (EQ), and C, the programming language in which it was written. This geochemical modeling software determines the saturation index of each mineral. The saturation index, or SI, of a mineral is defined by the following equation: $SI = \log(\frac{IAP}{Ksp})$, where SI is the saturation index, IAP is the ion activity product, and K_{sp} is the solubility product constant. The ion activity product is defined as the product of the activities of the ions in a given solution. Ion activity is similar to concentration, but it is corrected for ion-ion interactions in a solution. Ion activity product is affected by the concentration of ions in solution; as concentration increases, IAP increases, and that indicates that there are more ion-ion interactions in solution. K_{sp} , or the solubility product constant, represents the level at which a substance dissolves in a solution. K_{sp} is affected by the temperature of the solvent. A large K_{sp} indicates that a substance is very soluble in the solvent.

PHREEQC determines the saturation index of each mineral using the formula stated above. If IAP > K_{sp}, the river is supersaturated with respect to a given mineral, and the saturation index would be positive. If IAP = K_{sp}, then the solution is saturated, and the river and the mineral are in equilibrium. In this case, the saturation index would be zero. If IAP < K_{sp}, then the river is undersaturated with respect to a given mineral, and the river will dissolve more of that mineral in time. In this case, the saturation index would be negative.

Results

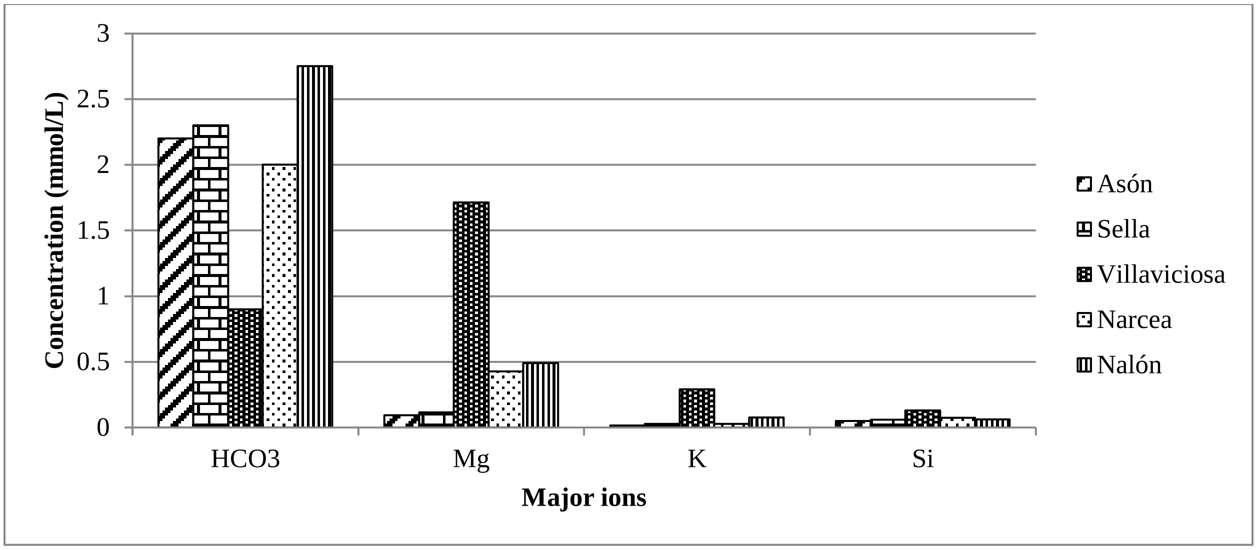
The ionic concentrations of the samples collected in 2011 are as follows:

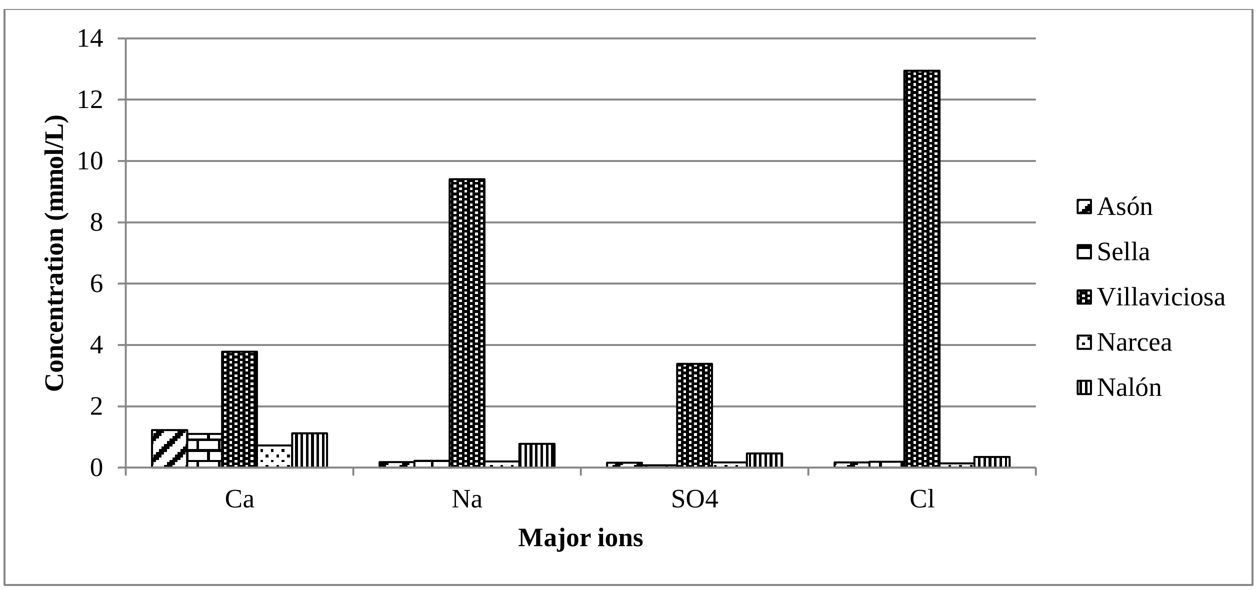
Table 1. The concentration of each ion in each river

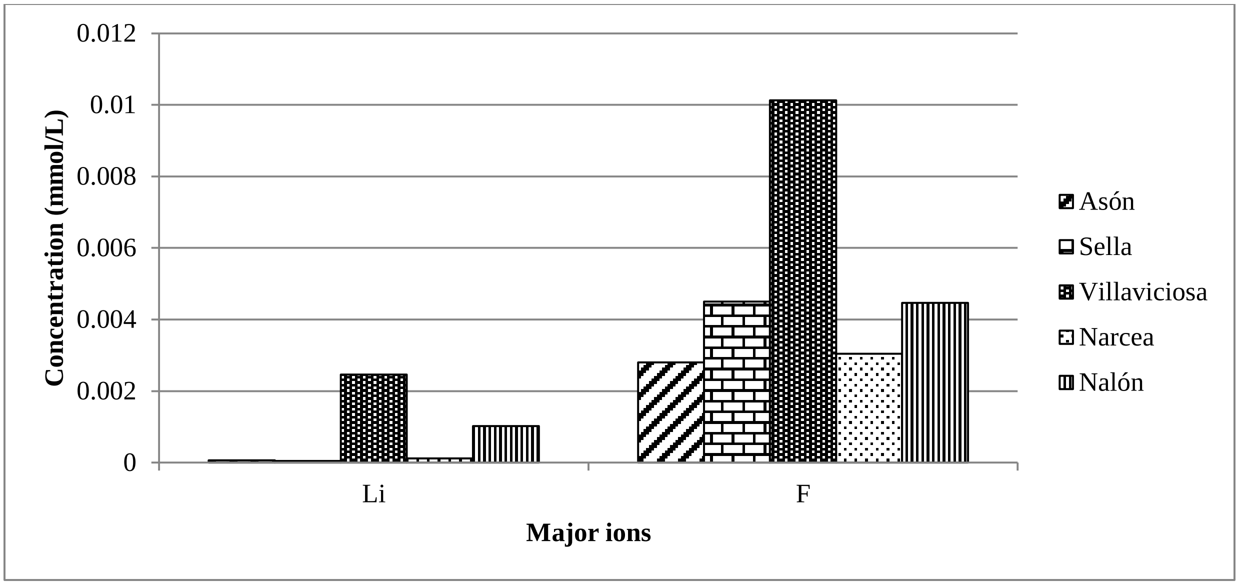
	Asón	Sella	Villaviciosa	Narcea	Nalón
Ca^{2+} (mmol/L)	1.22	1.10	3.78	0.719	1.12
Mg^{2+} (mmol/L)	0.0926	0.114	1.71	0.427	0.489
K^{+} (mmol/L)	0.0141	0.0274	0.290	0.0279	0.0766
Na^{+} (mmol/L)	0.180	0.221	9.41	0.201	0.776
Si (mmol/L)	0.0503	0.0595	0.129	0.0738	0.0608
Li^{+} (mmol/L)	$6.33x10^{-5}$	$4.97x10^{-5}$	$2.47x10^{-3}$	$1.22x10^{-4}$	$1.02x10^{-3}$
SO_4^{2-} (mmol/L)	0.159	0.0715	3.386	0.165	0.460
Cl^{-} (mmol/L)	0.172	0.187	12.9	0.137	0.343
F^{-} (mmol/L)	$2.80x10^{-3}$	$4.51\ x10^{-3}$	$1.01\ x10^{-2}$	$3.04\ x10^{-3}$	$4.47\ x10^{-3}$
Alkalinity (μeq/L)	2200	2300	900	2000	2750

In general, all of the rivers, except the Ría de Villaviciosa, exhibit similar trends in the concentrations. The concentrations of every ion are significantly higher in the Ría de Villaviciosa than the concentrations in any other river, except in the case of alkalinity. Figure 2 is a graphical comparison of the concentration of ions measured in each river.

Figure 2. A comparison of ionic concentrations in each of the five rivers.







The geochemical modeling results are in the appendix. The modeling suggests that four of the five rivers are close to being saturated with respect to quartz, while the fifth, the Ría de Villaviciosa, is oversaturated with respect to quartz. All of the rivers are close to saturation with calcite and aragonite, as well.

Discussion

All of the rivers except for the Ría de Villaviciosa are dominated by HCO_3^-. In addition to Figure 2 above, this relationship can also be seen in Figure 3. This method of comparison was described by Stallard and Edmond (1987). In this graph, the sum of the concentrations of Ca^{2+} and Mg^{2+} ions are compared to the concentration of bicarbonate. By looking at this relationship, it can be determined whether the river is dominated by bicarbonate. In Figure 3, four of the five rivers fall slightly above the $(Ca^{2+}+Mg^{2+})$:HCO_3^- 1:1 line, which indicates that there is a high influence of carbonate rocks on these rivers. The fifth river, the Ría de Villaviciosa, plots very far above this 1:1 line. This means that there is an excess source of calcium, and this source of calcium is contributing an anion that is not bicarbonate to these rivers. The Ría de Villaviciosa flows through an evaporite deposit, and this evaporite deposit contains both anhydrite and gypsum. Both anhydrite and gypsum contribute calcium to the system but contribute sulfate instead of bicarbonate. When calcium and magnesium are plotted against sulfate in Figure 4, all of the rivers plot above the $(Ca^{2+}+Mg^{2+}):SO_4^{2-}$ 1:1 line, but the Ría de Villaviciosa moves closer to the line, indicating that the sulfate ion is closer to equilibrium with calcium and magnesium than bicarbonate is. The other four rivers plot farther away from the 1:1 line in Figure 4 than in Figure 3, indicating that calcium and magnesium have a higher influence on these rivers than sulfate does.

Figure 5 shows the plot of $(Ca^{2+}+Mg^{2+}) = (HCO_3^-+SO_4^{2-})$. All of the rivers lie very close to, if not on, the $(Ca^{2+}+Mg^{2+}) = (HCO_3^-+SO_4^{2-})$ 1:1 line, except for the Ría de Villaviciosa. This suggests that bicarbonate and sulfate balance the calcium and magnesium in all of the rivers except for the Ría de Villaviciosa, which suggests that there is an additional source of calcium and magnesium to the Ría de Villaviciosa that does not contribute to the concentration of bicarbonate or sulfate; it is somewhat unclear what the source of the additional calcium and magnesium ions is. In this plot, however, the Ría de Villaviciosa lies the closest to the 1:1 line than in any other plot that looks at bicarbonate and sulfate.

Another comparison that helps determine what rocks are being weathered is the comparison of Na^+ and Cl^-. Elevated Na^+ concentrations suggest a substantial input from silicate minerals, while elevated Cl^- concentrations suggest weathering of evaporite minerals (Goldsmith et al., 2008). Rivers with an elevated Na^+ concentration plot above the $Na^+ = Cl^-$ line on Figure 6, and rivers with an elevated Cl^- concentration plot below the line. The Ría de Villaviciosa is the only river that flows through an evaporite deposit, and it is the only river that shows an elevated Cl^- concentration when compared to Na^+. The Ría de Villaviciosa plots below the $Na^+=Cl^-$ line in Figure 6. The Río Nalón has the highest ratio of Na^+ to Cl^-, which suggests that it has the most substantial input from silicate minerals out of all of the rivers.

A third comparison to help determine the weathering is that of (Na^++K^+ - Cl^-) versus Si. This was also used by Stallard and Edmond (1987). In their analysis of the Amazon basin, they suggest that a higher ratio of Si:(Na^++K^+ - Cl^-) corresponds with an increase in the rate of weathering (Stallard and Edmond, 1987). A high Si:(Na^++K^+ - Cl^-) ratio suggests that Si is leaching into the system due to an advanced degree of weathering (Goldsmith et al., 2008). The rivers with a high ratio are found below the 1:1 line in Figure 7. Two of the rivers fall below the 1:1 line. The first river, the Ría de Villaviciosa, plots in the negative, due to its high concentration of chloride; this river is not plotted in Figure 7 due to this fact. It is difficult to tell if it would plot below this line if the concentration of chloride was ignored, so the Ría de Villaviciosa will be ignored for further discussion. The Río Asón, which also falls below the 1:1 line, is slightly enriched in Si. According to Goldsmith et al. (2008), this could be due to a high degree of weathering causing silica to leach into the system, but it could also be due to the weathering of silicates that do not contain sodium and potassium. The rivers located above the 1:1 line (Sella, Narcea, and Nalón) have low Si:(Na^++K^+ - Cl^-) ratios. These low ratios suggest that there is mechanical weathering of soils in the watershed (Goldsmith et al., 2008). This mechanical weathering exposes new surfaces to the watershed, as well as new Na^+ and K^+, both of which are easily soluble in water (Goldsmith, 2008).

Figure 3. Plot of Ca^{2+}+Mg^{2+} vs. HCO_3^- in μeq/l in stream water

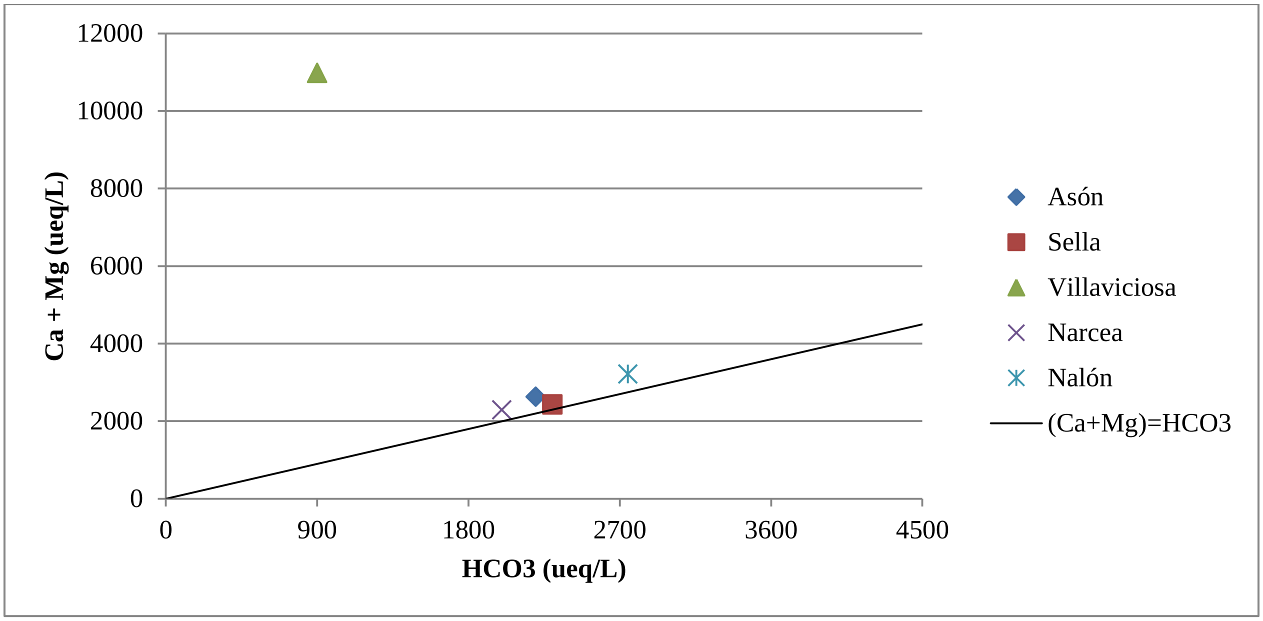


Figure 4. Plot of Ca^{2+}+Mg^{2+} vs. SO_4^{2-} in μeq/l in stream water

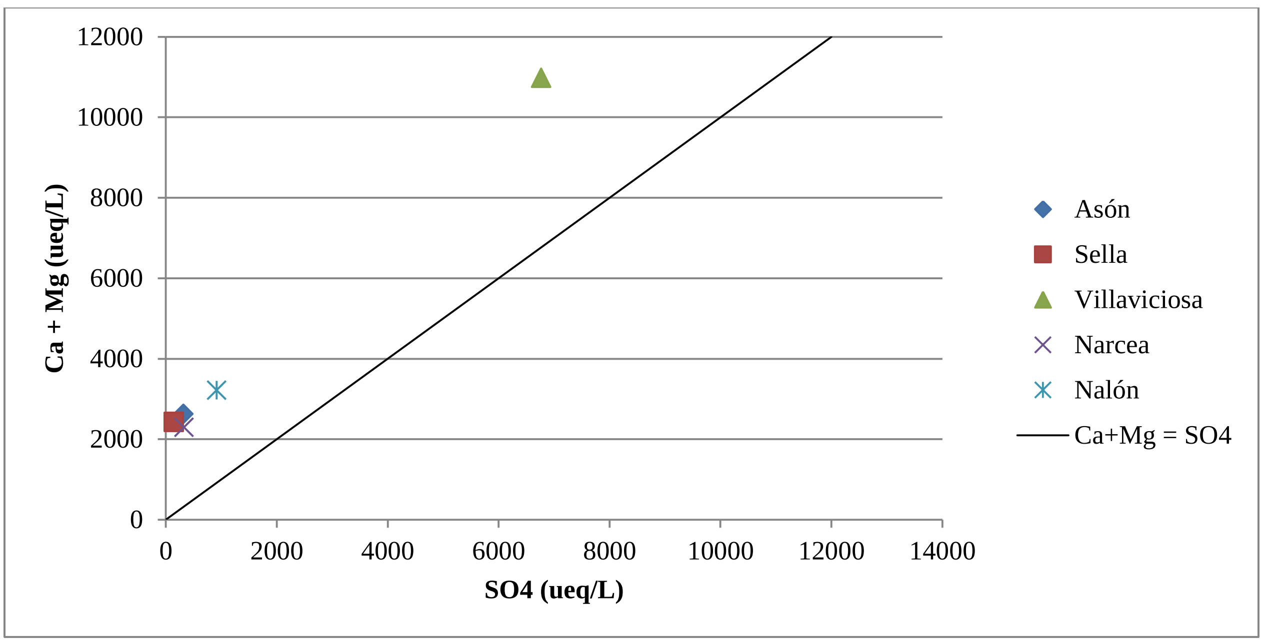


Figure 5. Plot of Ca^{2+}+Mg^{2+} vs. HCO_3^-+ SO_4^{2-} in μeq/l in stream water

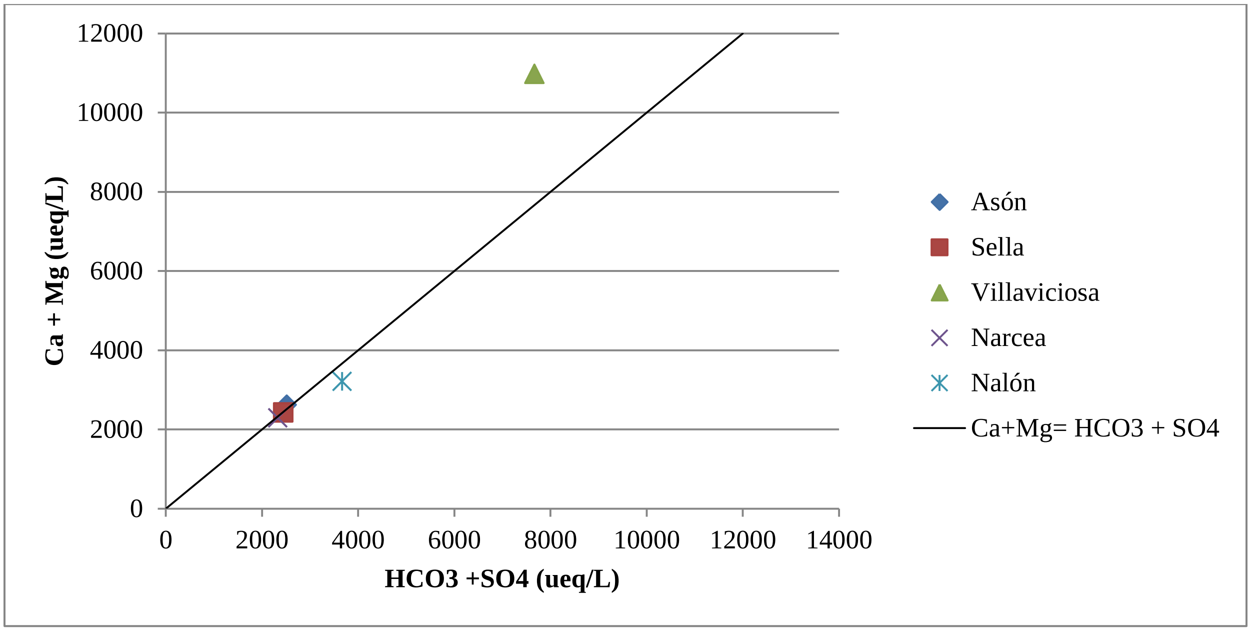


Figure 6. Plot of Na^+ vs. Cl^- in mmol/l in stream water.

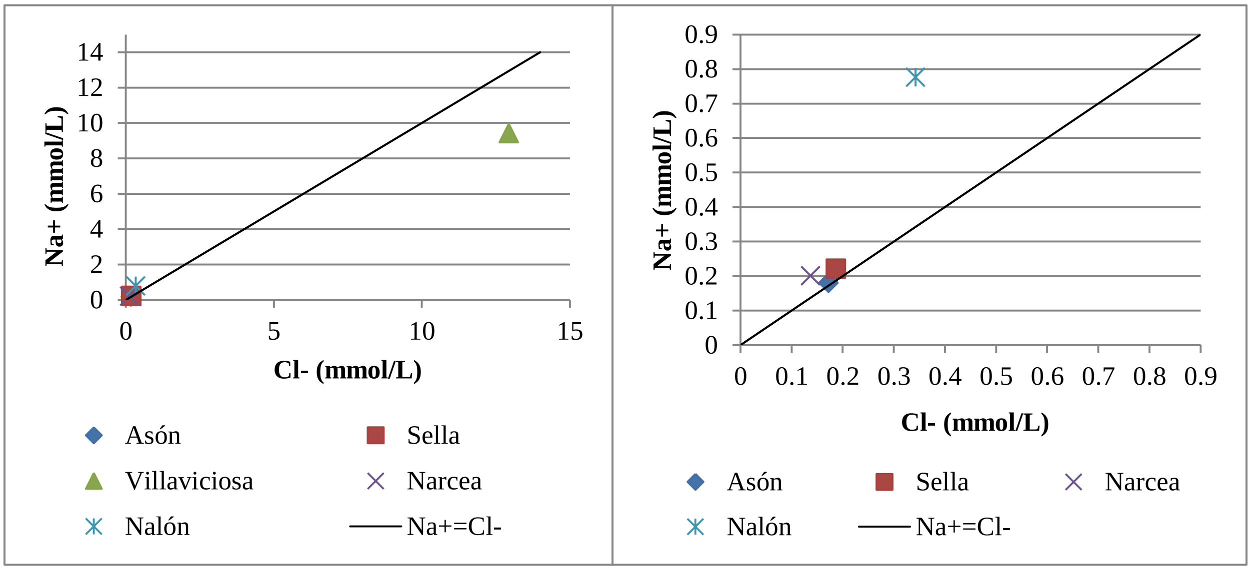
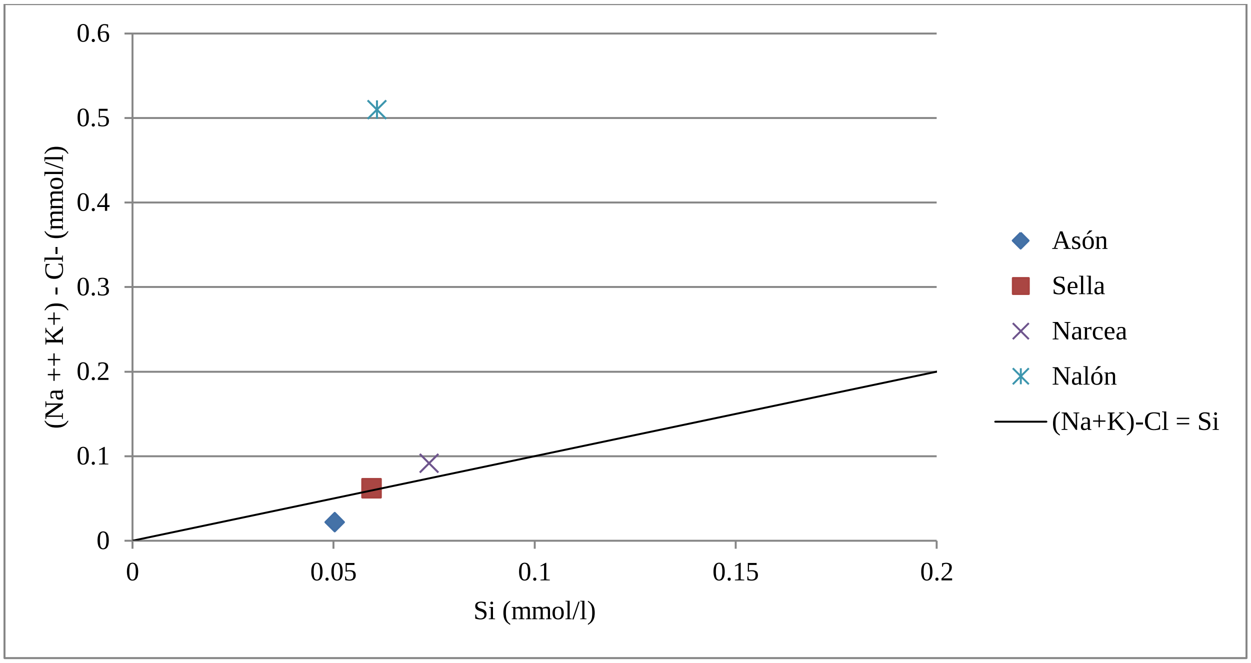


Figure 7. Plot of Na^{+}+K^{+} - Cl^{-} vs. Si in mmol/l in stream water



Although lithium does not make up a large percentage of the dissolved ions of each river, there is a noticeable difference among the concentration in each river. This range of concentrations can be seen numerically in Table 1 or graphically in Figure 2. The Ría de Villaviciosa has the highest concentration of Li^{+}, while the Asón and Sella have concentrations that are two orders of magnitude less than that.

Lithium is fairly common in the continental lithosphere; in fact, it is about as common as chlorine at 20-70 ppm (Warren, 2010). It is also widely distributed throughout Earth's crust, so it is not just found in large deposits in a few places throughout the world (Warren, 2010). However, lithium is commonly found in pegmatite and other igneous rocks, especially in the igneous mineral spodumene (Warren, 2010). These types of rocks are unlikely to be the source for lithium in northern Spain because the bedrock in this region is primarily made up of sedimentary rocks. There is, however, one small porphyritic dike through which the Río Narcea flows, but the makeup of that dike is not recorded on the geologic map.

In addition to igneous rocks, lithium can also be found in saline lacustrine settings in tectonically and magmatically active terrains (Warren, 2010). Northern Spain was, and still is, tectonically active, the area has a lot of faults, and there is a mountain range that spans across that region. Kesler et. al (2012) write that most current brine deposits are in geologically enclosed basins containing lacustrine deposits. Once the water in these brines evaporates, evaporite deposits are formed. It would be reasonable to assume that there was lithium in these brines, since northern Spain is a tectonically active region. If there was lithium in the brine, lithium would also be incorporated into the evaporite minerals through which the Ría de Villaviciosa flows. This would explain the relatively high concentration of lithium in this river compared to other rivers.

Lithium substitution is also an important source for lithium in these rivers. Lithium has an atomic radius of .68 Å, which makes it similar in size to magnesium and ferrous iron, which have atomic radii of .66 Å and .74 Å respectively (Chen, 1999). This means that lithium can be found in rocks that contain magnesium and rocks that contain iron. Lithium also preferentially bonds with silicates (Chen, 1999). In *Principles of Geochemistry*, Faure (1998) writes that sandstone contains 15 ppm of lithium, while carbonate rocks contain 5 ppm of lithium. The Río Nalón and the Río Narcea both flow through iron-containing sandstone. Lithium could have substituted for iron, so the lithium concentration of this iron-containing sandstone could be more than the 15 ppm of the average sandstone described by Faure (1998). None of the other rivers flows through iron-containing sandstone. The Río Nalón is also the only river that flows through shale, a rock that contains, on average, 66 ppm of lithium (Faure, 1998). Again, this could contribute to the high lithium content in that river.

It is also important to consider the presence of other minerals in the area that were not modeled by PHREEQC due to the lack of data. Aluminosilicate minerals, such as K-feldspar ($KA1Si_3O$) and plagioclase ($NaA1Si_3O$), are commonly found in sandstone, but the concentration of aluminum was not measured in any of these streams. Aluminum is only slightly soluble in water with circumneutral pH, so the concentration of aluminum in each river would be very low, and it would be reasonable to assume that the stable phase is $Al(OH)_3$ at equilibrium with the water (Faure, 1998). The equilibrium concentration is 1.91 x 10^{-7} mmol/L (Faure, 1998). If the aluminum information is added to other ion data using PHREEQC, it can model aluminosilicates that are also present in that area. The additional minerals, as determined by PHREEQC (Parkhurst & Appelo, 2013) are listed in the appendix.

Some of these minerals—Ca-montmorillonite, illite, and kaolinite—are products of weathering. A greater abundance of these minerals suggests a greater amount of weathering in a region. Although all of the rivers are severely undersaturated with respect to all of these aluminum-containing minerals, the Ría de Villaviciosa is the closest to equilibrium with respect to all of the clay minerals. This suggests the rocks being weathered by the Ría de Villaviciosa undergo the highest degree of weathering compared to all of the other rivers. The Río Narcea and the Río Nalón also have a relatively high influence of clay minerals, according to PHREEQC. This is likely because these two rivers flow through slate, and the Río Nalón flows through shale. Both of these rocks are made up of clay minerals, so it would make sense that clay minerals have a relatively high influence on the chemistry of these rivers.

Although the geochemical modeling results suggest that the Ría de Villaviciosa is oversaturated with quartz, this might not be true. The first explanation for this is that there is amorphous silica found in the evaporite deposits. Amorphous silica has the same formula as quartz, but it is not the same thing as quartz. Another explanation is the presence of aluminosilicate minerals such as K-feldspar and plagioclase. However, even when the aluminum data are added to the modeling, PHREEQC still reports that the Ría de Villaviciosa is oversaturated with quartz. This could be because the aluminum concentration is different than the assumed value. Another possibility is that there were other elements present in the river that were not measured while collecting samples. Those elements could be present in the water, due to weathering of other minerals besides quartz, but if they were not measured and not accounted for by PHREEQC, they would not be present in the geochemical modeling. This might decrease the saturation index of quartz.

The concentration of fluoride in these rivers also varies greatly. PHREEQC (Parkhurst and Appelo, 2013) suggests that the sole source of fluoride is from the mineral fluorite (CaF_2). Fluorite can be found in carbonate deposits, and it can also be found with gypsum (Nesse, 2000). Another source of the fluoride could be from the mineral sellaite, which has the chemical formula MgF_2 (Dana et al., 1997). This mineral can be found with anhydrite deposits, and in dolomite deposits (Dana et al., 1997). Fluorite and sellaite are not listed in any of the geologic maps of the area, but it is likely that they are found in the bedrock, since there are minerals with which they are commonly associated. Sellaite is not listed in PHREEQC's results because it is not in PHREEQC's database. Even if the mineral was found in the bedrock, PHREEQC would not list it because the program does not consider it when looking for minerals.

The Ría de Villaviciosa is the river with the most different chemistry, and it is only river that flows through an evaporite deposit. The Río Nalón also has a fairly different chemistry than the other rivers. The Río Nalón is the only river that flows through shale and kaolinite. It is also the only river that flows through a mine, which could contribute to the low Si:(Na^{+}+K^{+} - Cl^{-}) ratio, which suggests an increase in mechanical weathering. The other three rivers, the Río Asón, the Río de Sella, and the Río Narcea, have smaller differences in chemistry with respect to each other. The slight differences in the chemistries can be contributed to the slight differences in bedrock geology. Although they do flow through similar lithologies, there are differences, which can contribute to a difference in chemistry.

Conclusion

The aqueous chemistry of each river is affected by the bedrock geology of the region. The Ría de Villaviciosa flows through the most different lithology out of all of the rivers; it is the only river that flows through an evaporite deposit (Pignatelli, Giannini, Ramírez del Pozo, Beroiz, & Barón, 1972; Beroiz, Barón, Ramirez del Pozo, Giannini, & Gervilla, 1972). Its chemistry is also significantly different than all of the other rivers due to its unique geology. The Río Nalón also has chemistry that is different than the other rivers, and it is the only river that flows through shale and kaolinite.

The other rivers flow through fairly similar lithologies, and their chemistry is all fairly similar. There are differences in the chemistry of each river, however, and that is because of the slight differences in lithologies. For example, the Río Narcea flows through iron-containing sandstone, and the Río Sella and the Río Asón do not. The amount of sandstone when compared to limestone and dolomite can affect the chemistry of the water, and the relative amounts of the rock types are difficult to tell based on the map alone.

Geochemical modeling suggests that all of the rivers are undersaturated with respect to every mineral, except one. The Ría de Villaviciosa is oversaturated with respect to quartz, and it is the only river that is oversaturated with any mineral. However, this could be misleading, since quartz is very resistant to weathering, and there might be other minerals being weathered than PHREEQC suggests. All of the rivers are closest to saturation with carbonate and silicate minerals. In the Ría de Villaviciosa, halite, gypsum, and anhydrite have higher saturation indices—that is, less negative—than the other rivers. This is because it is the only river that flows through an evaporite deposit.

All of the results from this study suggest that there is a relationship between the bedrock geology and the chemistry of each river. Three of the five rivers flow through very similar lithologies of carbonate and sandstone, and their chemistries are fairly similar. The Nalón is similar to the other three, but its chemistry is slightly different, probably due to the presence of shale in the bedrock. The final river, the Ría de Villaviciosa, has a very different lithology and a very different chemistry. The differences in lithologies of the rivers can be seen on the maps, and those differences are reflected by the differences in chemistries of the rivers.

Recommendations for future work

The water samples in this region were only taken one time. It would be interesting to see whether the ion concentrations vary depending on the season, and if they do vary how much they vary by. It would also be useful to measure the concentration of aluminum and iron, since those two ions were not measured in this study. Thirdly, it would be useful to collect rock samples because some of the rocks that are in this region might not be represented in the geologic maps of the area.

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APPENDIX

Table 1A. Summary of map 13

Map 13: Avilés: Mouth of Nalón			
Letter/Number	Period	Makeup	Formation
QA	Quaternary	Alluvial and river deposits	N/A
$S_1^B - D_{11}$	Silurian-Devonian	Iron-containing sandstone	Furada

(Julivert, Truyols, Marcos, & Arboleya, 1972)

Table 2A. Summary of map 15

Map 15: Lastres: Ría de Villaviciosa			
Letter/Number	Period	Makeup	Formation
Q	Quaternary	Alluvial fans and "scree cones"	N/A
$T_{G2\text{-}3}$	Triassic	Red clay and evaporites, calcite conglomerate, and calcite	N/A
$J_{11\text{-}21}^{0\text{-}2}$	Jurassic	Calcite and dolomite	N/A

(Pignatelli et al., 1972)

Table 3A. Summary of map 28

Map 28: Grado: Intersection of Narcea and Nalón Narcea:			
Letter/Number	Period	Makeup	Formation
Qc	Quaternary	Colluvium	N/A
D_{11}-D_{13}*	Devonian	1. Limestones, loam, and slate 2. Limestone, dolomite 3. Limestone, slate	1. Arnao 2. Ferroñes 3. Nieva (All part of the Rañeces Group)
D_{13}-D_{21}	Devonian	Limestone, slate	Moniello
D_{21}-D_{22}	Devonian	Iron containing sandstone	Naranco
D_{22}-D_{31}	Devonian	Limestone, slate	Candás
D_{31}-D_{32}	Devonian	Sandstone with iron-containing zones	Candás

Letter/Number	Period	Makeup	Formation
H_{1}^{A}	Lower Carboniferous	Limestone and red slate Slate and white limestone	Griotte-Sella-Alba
H_{1-21}^{B-B}	Upper Carboniferous	Gray sandstone	Montaña
Qt	Quaternary	Terraces	N/A
FO		Porphyritic dike	N/A

*located near a thrust fault

Nalón:

Letter/number	Period	Makeup	Formation
H_{1-23}^{B-B}	Carboniferous	Slate, sandstone, limestone.	N/A
QAl	Quaternary	Alluvium	N/A
T_{C2-31}^{Ac-A3}	Tertiary	Marl/loam, clay, white limestone	N/A
O_1** (Mine region)	Ordovician	White quartzite	Cabos-Amoric-Barrios
O_1^P	Ordovician	Slate with kaolinite zones	N/A
CA_1-O_1	Cambrian/Ord.	Slate and quartzite	Oville
S_{A-B}^{1-1}	Silurian	Black shale	N/A
Qc	Quaternary	Colluvium	N/A
D_{11}-D_{13}*	Devonian	1. Limestones, loam, and slate 2. Limestone, dolomite 3. Limestone, slate	1. Arnao 2. Ferroñes 3. Nieva (All part of the Rañeces Group)
D_{13}-D_{21}	Devonian	Limestone, slate	Moniello
D_{21}-D_{22}	Devonian	Iron containing sandstone	Naranco
D_{22}-D_{31}	Devonian	Limestone, slate	Candás
D_{31}-D_{32}	Devonian	Sandstone with iron-containing zones	Candás
H_{1}^{A}	Lower Carboniferous	Limestone and red slate Slate and white limestone	Griotte-Sella-Alba
H_{1-21}^{B-B}	Upper Carboniferous	Gray sandstone	Montaña
Qt	Quaternary	Terraces	N/A

*Located near a thrust fault

(Instituto Geológico y Minero de España, 1972a)

Table 4A. Summary of map 30

Map 30: Villaviciosa: Ría de Villaviciosa (and its tributaries)			
Letter/Number	Period	Makeup	Formation
Q	Quaternary	Alluvial fans and “scree cones”	N/A
T_{G2-3}	Triassic	Red clay and evaporites	N/A
T_{G1-2}	Triassic	Conglomerate and red sandstone	N/A
P*	Permian	Conglomerate, sandstones, marl, slate, and evaporites	N/A
H^{B-B*}_{21-24}	Carboniferous	Slate, sandstone, calcite, and coal	N/A
*Located near faults and anticlines			

(Beroiz et al., 1972)

Table 5A. Summary of map 31

Map 31: Ribadesella: Mouth of Sella			
Letter/Number	Period	Makeup	Formation
24	Quaternary	Silt, mud, lutite-- Tidal flat	N/A
25	Quaternary	Sand--Beach	N/A
23	Quaternary	Gravels, sand, and silt-- alluvium	N/A
20	Quaternary	Conglomerate, gravel, and sand—fluvial terraces	N/A
14	Jurassic	Dolomite, limestone, and rhythmites with calcareous marl	Gijón and Rodiles
3*	Ordovician	Paraconglomerate, white quartzite, sandstone, and siltstone	Barrios
2	Cambrian/Ordovician	Lutites, sandstone with glauconite and quartz	Oville
1**	Cambrian	Dolomites, limestone, and sandstone with glauconite	Lancara
9	Carboniferous	Black calcite with parallel lamination and sedimentary breccia	Barcaliente
17	Cretaceous	Quartzarenite, sandstone, limestone, and siltstone	N/A
*located near a fault **located near a thrust fault			

(Navarro & Rodríguez Fernández, 1972)

Table 6A. Summary of map 36

Map 36: Castro-Urdiales: Mouth of Limpias (Asón)			
Letter/Number	Period	Makeup	Formation
Q_2M	Quaternary	Marsh	N/A
Q_2Al	Quaternary	Alluvium	N/A
C^{0-12}_{15-16}	Cretaceous	Limestone with rudists and forams	N/A
C^{3-0}_{w12-14}	Cretaceous	Sandstone and silty clays	N/A

(Olivé Davó, Martín Alafont, Ramírez del Pozo, & Portero García, 1972)

Table 7A. Summary of map 60

Map 60: Valmaseda: Asón (meets up with Carranza and Gándara)			
Letter/Number	Period	Makeup	Formation
Q_T	Pleistocene	Terrace	N/A
Q_2Al	Quaternary	Alluvium	N/A
Letter/Number	Period	Makeup	Formation
C^{12}_{p12}	Cretaceous	Limestone with oysters and bryozoans	N/A
C^{3-0}_{w12-14}	Cretaceous	Sandstone and silty clays	N/A
J_{p33}-C_{p11}	Jurassic-Cretaceous	Conglomerate, sandstone, clay, and lacustrine limestone	N/A
J_2	Jurassic	Microcrystalline limestones, clayed limestone, marl	N/A
C^{1-3}_{153-15}	Cretaceous	Marl, sand lenses	N/A

(Instituto Geológico y Minero de España, 1972b)

Table 8A. Geochemical modeling results from PHREEQC

Mineral name	Mineral formula	Asón	Sella	Villaviciosa	Narcea	Nalón
Anhydrite	$CaSO_4$	-2.66	-3.04	-1.24	-2.86	-2.30
Aragonite	$CaCO_3$	-0.73	-0.75	-0.86	-1.00	-0.71
Calcite	$CaCO_3$	-0.59	-0.61	-0.72	-0.85	-0.57
Chalcedony	SiO_2	-0.75	-0.67	-0.33	-0.58	-0.66
Chrysotile	$Mg_3Si_2O_5(OH)_4$	-11.29	-10.86	-7.25	-8.96	-9.06
CO_2 (g)	CO_2	-1.87	-1.85	-2.31	-1.91	-1.78
Dolomite	$CaMg(CO_3)_2$	-2.17	-2.07	-1.66	-1.80	-1.36
Fluorite	CaF_2	-3.62	-3.25	-2.33	-3.78	-3.31
Gypsum	$CaSO_4$:$2H_2O$	-2.44	-2.82	-1.02	-2.64	-2.08
H_2 (g)	H_2	-22.00	-22.00	-22.00	-22.00	-22.00
H_2O (g)	H_2O	-1.51	-1.51	-1.51	-1.51	-1.51
Halite	NaCl	-9.15	-9.03	-5.63	-9.20	-8.23
O_2 (g)	O_2	-39.19	-39.19	-39.19	-39.19	-39.19
Quartz	SiO_2	-0.34	-0.27	0.07	-0.18	-0.26
Sepiolite	$Mg_2Si_3O_{7.5}OH$:$3H_2O$	-8.99	-8.57	-5.60	-7.15	-7.36
Sepiolite (d)	$Mg_2Si_3O_{7.5}OH$:$3H_2O$	-11.89	-11.47	-8.50	-10.05	-10.26
SiO_2 (a)	SiO_2	-1.59	-1.51	-1.17	-1.42	-1.50
Talc	$Mg_3Si_4O_{10}(OH)_2$	-9.09	-8.51	-4.21	-6.42	-6.69

Table 9A. Geochemical modeling results with aluminum concentration added in

Mineral name	Formula	Asón	Sella	Villaviciosa	Narcea	Nalón
$Al(OH)_3$(a)	$Al(OH)_3$	-4.92	-4.92	-4.96	-4.92	-4.93
Albite	$NaAlSi_3O_8$	-8.45	-8.15	-5.57	-7.91	-7.58
Alunite	$KAl_3(SO_4)_2(OH)_6$	-14.80	-15.19	-11.39	-14.44	-13.22
Anorthite	$CaAl_2Si_2O_8$	-11.50	-11.39	-10.44	-11.39	-11.42
Ca-Montmorillonite	$Ca_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$	-8.05	-7.79	-6.57	-7.48	-7.77
Chlorite (14A)	$(Mg,Fe)_3(Si,Al)_4O_{10}$	-20.34	-19.64	-13.80	-16.50	-16.66
Gibbsite	$Al(OH)_3$	-2.23	-2.23	-2.27	-2.23	-2.24
Illite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O10[(OH)_2,(H_2O)]$	-9.65	-9.20	-7.26	-8.72	-8.77
K-feldspar	$KAlSi_3O_8$	-6.99	-6.48	-4.51	-6.19	-6.02
K-mica	$KAl_2(AlSi_3O_{10})(F,OH)_2$	-5.84	-5.33	-3.43	-5.04	-4.88
Kaolinite	$Al_2Si_2O_5(OH)_4$	-4.27	-4.13	-3.52	-3.94	-4.12